Magnetic and Electric Field Effects on the Optical Spectra of Molecular Crystals

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Magnetic and Electric Field Effects on the Optical Spectra of Molecular Crystals

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Hauptvortrag

Absorptionsspektren, von Kristallen / Absorptionsspektren, sichtbar und ultraviolett / Dipolmoment / Magnetismus

A compact review is given of the use of the Zeeman and Stark effect in the study of the low temperature optical spectra of molecular solids.

In einer kompakten Übersicht wird der Nutzen des Zeeman- und des Stark-Effektes für das Studium von optischen Tieftemperaturspektren von molekularen Festkörpern gezeigt.

1. Introduction

Since the first demonstration of magnetic [1] and electric [2] field effects on optical spectra, techniques based on these perturbations have become the major tools of spectroscopists to extract maximum information from spectral events.

While the Zeeman and Stark effects were already fully exploited in studies of atomic species in the gas and condensed phase [3] spectroscopic studies of molecular solids were still to come. It was only after the pioneering work of Davydov [4] that the study of molecular solids advanced. The high resolution optical experiments by McClure [5] on the naphthalene-durene mixed crystal further showed the linewidth of molecular and atomic optical transitions to be comparable. This fact assured the success to come of the application of magnetic and electric fields in the study of the optical properties of molecular solids.

2. Zeeman Effect

As the Zeeman effect derives from the interaction between a magnetic moment and a magnetic field it is a useful tool only in spectroscopic studies of those electronic transitions that involve an effective change of magnetic moment. In molecular crystals, singlet-triplet transitions belong to this category, and Zeeman effect studies on these excitations, mainly performed by Hochstrasser and co-workers [6], have provided us with many important new molecular and crystal excited state properties as:

1. triplet state orbital assignment.
2. spin-orbit coupling route(s)
3. sign (and magnitude) of ZFS parameters
4. sign and magnitude of factor group splitting.

Singlet orbitally-degenerate singlet transitions are another category that can be advantageously studied using the Zeeman effect. The recent Zeeman absorption experiments on porphyrins in Spolski'i matrices by Canters et al. [7] show how much can be learned of the excited state properties of these species. We will now briefly review the basic underlying principles of the Zeeman effect measurements on singlet-triplet transitions in molecular crystals.

Consider therefore the effect of a magnetic field on the zero field spin substates $\tau_i (i = x, y \text{ or } z)$ of an isolated triplet excited molecule in a space fixed lattice. The well known hamiltonian ($\boldsymbol{H}_m$) governing this situation is the following:

$$\boldsymbol{H}_m = \boldsymbol{H}_0 - \{X S_x^2 + Y S_y^2 + Z S_z^2\} + \beta \boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S} . \quad (1)$$

$\boldsymbol{H}_0$ contains all the information that specifies the spatial part of the excited state level in question, X, Y and Z are the fine-structure principal values, and $\beta \boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S}$ is the Zeeman interaction perturbation. The matrix elements of H_m in the basisset τ_i are easily found and can be compactly written as:

$$\langle \tau_i | \boldsymbol{H}_m | \tau_j \rangle = I \delta_{ij} - i \operatorname{sgn}(i \times j) g_{|i \times j|} \beta B_{|i \times j|} ; \quad I = X, Y \text{ or } Z . \quad (2)$$

For purpose of further discussion the level ordering $Z > Y > X$ is accepted and the magnetic field is further assumed to be parallel to the molecular z-axis.

There are two limits of magnetic field strength that are of spectroscopic interest and these will be considered now:

i) $$g_{zz} \beta B_z = \frac{1}{2} (9Z^2 - (X - Y)^2)^{1/2} \ll \Delta \upsilon \text{ (optical linewidth)} \quad (3a)$$

or in terms of the zero field splitting parameters D and E:

$$g_{zz} \beta B_z = ((D + E)(D - E))^{1/2} . \quad (3b)$$

In this situation the spin sub levels $|y\rangle$ and $|z\rangle$ anticross [8] and the states can be best described as:

$\alpha |z\rangle + \beta |y\rangle$ and

$-\beta |z\rangle + \alpha |y\rangle$ where

α and β are rapidly varying functions of $\boldsymbol{B}$ in the neighbourhood of the anticrossing point. It can be shown [8] that in general one can expect, at low temperature, where the $|z\rangle$ and $|y\rangle$ spin sublevels are effectively isolated, modulation of the phosphorescence to occur when the magnetic field is sweeped through the anticrossing region. These effects can thus be used to measure the excited state fine structure parameters [8, 9]. The main disadvantage of this method lies in the necessary precise (within $\sim 1°$) alignment of the magnetic field along principal molecular directions in order to observe these LAC signals.

ii) $g_{zz} \beta B_z > \Delta \upsilon > Z ; \quad X - Y .$

When the Zeeman splitting exceeds the optical linewidth ($\Delta\nu$), one often observes an intensity imbalance among the Zeeman components.

This effect is caused by the mixing of the high field Zeeman states through the fine structure perturbation and thus can be used to calculate the molecular fine-structure parameters. Using first order perturbation theory the unnormalized Zeeman states are calculated to be:

$$\begin{aligned} |1'\rangle &= |1\rangle + \alpha|-1\rangle \\ |-1'\rangle &= |-1\rangle - \alpha|1\rangle \end{aligned} \qquad \alpha = \frac{X - Y}{4 g_{zz} B} \tag{4}$$

from which the intensity ratio of the Zeeman components is calculated to be [10]

$$\frac{I(+1')}{I(-1')} = \left(\frac{1+\alpha}{1-\alpha}\right)^2 . \tag{5}$$

This expression shows that the accuracy of this method in determining fine structure parameters is low, unless these parameters are exceptionally large. The main use of the Zeeman effect in the study of singlet-triplet transitions concerns the assignment of the spin-orbit active level(s) of the excited state. For the magnetic field $\boldsymbol{B}$ parallel to the molecular z-axis the high field transition moments for absorption from the ground state into the Zeeman components are calculated to be:

$$\dot{\boldsymbol{m}}_{\pm 1} = 2^{-1/2}(\dot{\boldsymbol{m}}_x \pm i\dot{\boldsymbol{m}}_y) \quad \text{and} \quad \dot{\boldsymbol{m}}_0 = \dot{\boldsymbol{m}}_z . \tag{6}$$

The zero field transition moments m_x, m_y and m_z can be further expanded as:

$$\dot{\boldsymbol{m}}_x = f_{xx}\hat{\boldsymbol{x}} + f_{xy}\hat{\boldsymbol{y}} + f_{xz}\hat{\boldsymbol{z}} \tag{7}$$

where f_{ij} are spin-orbit coupling matrix elements that connect spin substate τ_i with singlet states polarized along the j-direction. In a polarized Zeeman experiment the projection of the $\dot{\boldsymbol{m}}_{\pm 1}$ and $\dot{\boldsymbol{m}}_0$ moments along the direction of polarization ξ_k are considered:

$$|\dot{\boldsymbol{m}}_{\pm 1} \cdot \xi_k|^2 \quad \text{and} \quad |\dot{\boldsymbol{m}}_0 \cdot \xi_k|^2 \tag{8}$$

and with one of the matrix elements f_{ij} quite often being dominant these experiments are easily interpreted; e.g. in the above mentioned case with $\dot{\boldsymbol{m}}_x = f_{xx}\hat{\boldsymbol{x}}$, all other f_{ij} elements being zero, the Zeeman spectrum only shows the $m_{\pm 1}$ components and only for x polarized radiation. In general the spatial symmetry (electronic $\otimes$ vibronic) of a given level $|l\rangle$ is determined via the relation:

$$\Gamma_{|l\rangle} = \Gamma_{\tau_i} \otimes \Gamma_{r_k} . \tag{9}$$

Herein is Γ_{τ_i} the representation of the spin-orbit active level τ_i (determined from the Zeeman pattern) and Γ_{r_k} the representation of the vector r_k that is parallel to the spin-orbit induced transition moment (determined with polarized (ξ_k)) radiation. So far we have assumed to deal with isolated triplet states: e.g. a triplet state of an isolated guest molecule in an optically inert host crystal. The oscillator strength of most singlet-triplet transitions however is usually so small that for optical absorption studies pure crystals have to be used. In pure solids one deals with exciton rather than molecular levels and the effect of intermolecular forces on the Zeeman spectra needs to be considered. The discussion is now further restricted to the special case of a molecular solid that contains 2 molecules in the unit cell and the b-axis as symmetry axis.

In the limit where the intermolecular interactions dominate the fine structure splittings (which is usually the case) the optically accessible ($k = 0$) crystal states can be best described as ${}^3\Psi^f_{\pm} T_\mu$, where ${}^3\Psi^f_{\pm}$ are the triplet factor group states $2^{-1/2}({}^3\varphi^f_\alpha \pm {}^3\varphi^f_\beta)$ and T_μ the crystal spin substates. $T_\mu = \sum_i C_{\mu i}\tau_i \cdot \mu = a^*, b, c^*$ and $i = x, y$ and z. Herein is C a matrix that geometrically relates the molecular (τ_i) with the crystal (T_μ) spin functions. These factor group states ${}^3\Psi^f_{\pm} T_\mu$ are induced through spin-orbit coupling with allowed uniquely polarized singlet factor group states. It can be shown [6] that in the case of one molecular active spin-orbit level the b-polarized intensity is proportional to:

$$I^f_b(T_\mu \pm) \alpha |\langle {}^1\Psi^s_+ | \boldsymbol{H}_{so} | {}^3\Psi^f_{\pm} T_\mu \rangle \mu_s(+) \cdot \hat{b}|^2 \tag{10a}$$

while the perpendicular b-polarized intensity can be written as:

$$I^f_{b\perp}(T_\mu \pm) \alpha |\langle {}^1\Psi^s | \boldsymbol{H}_{so} | {}^3\Psi^f_{\pm} T_\mu \rangle \mu_s(-) \cdot \hat{b}_\perp|^2 . \tag{10b}$$

Herein is $\boldsymbol{H}_{so} = \boldsymbol{h}_{so}(\alpha) + \boldsymbol{h}_{so}(\beta)$ the crystal spin-orbit coupling operator, ${}^1\Psi^s_{\pm}$ the mixing singlet with transition-moment $\mu_s(\pm)$ and $\hat{b}$ and $\hat{b}_\perp$ unit vectors in the direction of polarization of the exciting light. These expressions show that the exciton states $|T_{a^*}-\rangle$, $|T_{c^*}-\rangle$ and $|T_b+\rangle$ can only be observed for light polarized parallel to the crystal b-axis. The remaining crystal states $|T_{a^*}+\rangle$, $|T_{c^*}+\rangle$ and $|T_b-\rangle$ are polarized perpendicular to the b-axis according to Equation (10b). With a magnetic field along the crystal b-axis and polarized radiation one is thus able to separate the $|T_b+\rangle$ and $|T_b-\rangle$ factor group states from the other mixed ones, even if these are within the optical linewidth. Such experiments can therefore be used to determine sign and magnitude of the intermolecular translational inequivalent interactions and fine structure parameters [11]. These experiments obviously also yield information about the activity of the crystal spin-orbit axes that can be related to the molecular levels. In the case of suitable (uniaxial) molecular crystals high resolution magnetic circular (mcd) measurements can also be used to probe the spin-activity of the spin-orbit axes [12]. Such measurements could be extremely useful in the study of transitions where the Zeeman effect is doubtful [13] or within the optical linewidth.

3. Stark Effect

The Stark effect is basically due to the interaction between an electric dipole moment (odd parity) and an electric field. This implies that first order Stark effects are only to be expected in electronic states of non centro-symmetric molecules or in degenerate states of mixed parity [14]. Stark effect measurements thus enable us to probe the nett effect of the charge distribution in excited states of molecules and this is of great interest as most of our chemical intuition for reactions relates "to rule of the thumb" ideas of electron density distribution. Especially the interpretation of photochemically induced reactions could profit from an increased knowledge of excited state charge distributions.

We restrict ourselves to a discussion of the Stark effect on molecular solids at low temperature, where rotations are

frozen and the initial state is the groundstate. Again it is useful to first discuss the Stark effect on isolated molecules and than on pure crystals. Throughout this further discussion we again assume to deal with a molecular solid containing 2 molecules in the unit cell and with a b-axis as symmetry axis. The interaction between a dipole moment (permanent and induced) of a state $|k\lambda\rangle$ and a local electric field $\boldsymbol{F}$ can be written as:

$$V_{k\lambda}(\boldsymbol{F}) = -\boldsymbol{\mu}_{k\lambda}\cdot\boldsymbol{F} - \frac{1}{2}\boldsymbol{F}\cdot\boldsymbol{\alpha}_{k\lambda}\cdot\boldsymbol{F} \tag{11}$$

wherein $|k\lambda\rangle$ is a vibronic level (k electronic, λ vibrational designation), $\boldsymbol{\mu}_{k\lambda}$ the permanent electric dipole moment, $\boldsymbol{\alpha}_{k\lambda}$ the polarizability tensor of the level $|k\lambda\rangle$ in question and $\boldsymbol{F}$ the local electric field at the molecular site. When a polar guest molecule is now embedded in a non-polar host crystal, and this is the way most Stark effect measurements are done, translational equivalent host lattice sites contain guest molecules with oppositely phased dipole moments. From Equation (11) the Stark induced spectral shift for a transition $\langle k\lambda| \leftarrow |00\rangle$ is found to be (up to second order):

$$\Delta\upsilon_{00}^{k\lambda} = -(\boldsymbol{\mu}_{k\lambda} - \boldsymbol{\mu}_{00})\cdot\boldsymbol{F} - \frac{1}{2}\boldsymbol{F}\cdot(\boldsymbol{\alpha}_{k\lambda} - \boldsymbol{\alpha}_{00})\cdot\boldsymbol{F}. \tag{12}$$

This expression shows that the shift caused by the change in permanent dipole moment is sensitive to the polarity of the electric field while the induced dipole moment shift part is not. In an electric field therefore, say along the crystal b-axis, the *orientational* degeneracy is lifted and a splitting of the absorption (emission) line of magnitude $2|(\boldsymbol{\mu}_{k\lambda} - \boldsymbol{\mu}_{00})\cdot\boldsymbol{F}|$ is observed. For a local electric field of 10^5 V/cm aligned along a dipole moment change ($\Delta\boldsymbol{\mu}_{00}^{k\lambda}$) of 1 D this splitting is calculated to be 3.4 cm^{-1} and this is easily detectable for most electronic transitions. The second order electric field induced shift for an electric field of 10^5 V/cm along a direction of polarizability change $\Delta\alpha_{00}^{k\lambda} = 10$ Å^3 is only $2.8\cdot10^{-3}$ cm^{-1} (84 MHz) and this can be observed in a modulation type experiment [15]. Hochstrasser and Noe [16] were the first who realized a high resolution Stark effect measurement on a molecular crystal. Since then numerous Stark effect measurements have been performed aimed at measuring excited state dipole moments [17].

The main difficulty in extracting quantitative data from Stark effect measurements relates to the uncertainty of the local electric field. In the early experiments the Lorentz local field approximation: $\boldsymbol{E}_{\text{eff}} = \frac{n_i^2+2}{3}\boldsymbol{E}_{\text{appl}}$ [13] where n_i is the index of refraction along direction i, was used. Recent experiments by Hanson and Chen [18] showed this approximation for anisotropic organic solids to be inadequate and suggestions have been made to improve the local field calculation [19]. Stark effect measurements can also be used as an aid in the analysis of complex spectra [20, 21] where the variation in dipole moment change is used to probe different electronic states.

In centrosymmetric molecules there is only a second order Stark effect and only in case of nearby electronic states, e.g. the g and u $n\pi^*$ states of p-benzoquinone the "polarizability changes" can be physically interpreted [21]. If such states are absent, the polarizability tensor

$$\boldsymbol{\alpha}_{k\lambda} = 2\sum_{l,j\neq k,\lambda}\frac{\langle k\lambda|\hat{\boldsymbol{p}}|lj\rangle\langle lj|\hat{\boldsymbol{p}}|k\lambda\rangle}{E_{lj} - E_{k\lambda}}, \tag{14}$$

where $\hat{\boldsymbol{p}}$ is the dipole moment operator, truly manifests the electric field coupling of state $|k\lambda\rangle$ with all states $|lj\rangle$ of the proper symmetry. Meyling and Wiersma [15] recently reported preliminary results of second order Stark effect measurements on the origins of the lowest singlet state absorptions of tetracene and pentacene as guests in p-terphenyl. In these molecules the electric field effects are found to be exclusively due to polarizability changes on excitation and electric field induced intensity changes were not observed. Although these high resolution techniques seem promising in measuring the full anisotropy of the polarizability and transition polarizability tensor, much more work needs to be done to facilitate comparison with results obtained from solution spectra [22]. In pure solids the exciton states reflect the crystal space rather than the molecular symmetry. This means that in non polar crystals composed of polar molecules only second order Stark effects [23] can be observed. The electric field induced coupling among the exciton levels $\langle i\mu|$ and $|j\upsilon\rangle$, where i and j are electronic and μ and υ vibrational factor group states, is proportional to:

$$\langle i\mu|\hat{\boldsymbol{e}}\cdot\hat{\boldsymbol{p}}|j\upsilon\rangle = \boldsymbol{p}_{i\upsilon}^{i\mu}\delta_{\hat{\boldsymbol{e}},i\mu\otimes j\upsilon}\hat{\boldsymbol{e}}\cdot\hat{\boldsymbol{r}}_{i\mu\otimes j\upsilon}. \tag{15}$$

Herein is $\boldsymbol{p}_{j\upsilon}^{i\mu}$ the electric dipole (transition) moment among the relevant states and $\hat{\boldsymbol{e}}$ a unit vector in the direction of the applied electric field (E) which, in case of a non vanishing matrix element, should project unto the polar vector $\hat{\boldsymbol{r}}_{i\mu\otimes j\upsilon}$ that transforms like the direct product of $i\mu$ and $j\upsilon$. Equation (15) clearly shows that in centro symmetric crystals the diagonal elements of the Stark effect cancel and the field induced splitting ($2\Delta\upsilon(\boldsymbol{F})$) for the case of 2 molecules in the unit cell will be:

$$\Delta\upsilon(\boldsymbol{F}) = (V_{\alpha\beta}^2 + |\boldsymbol{F}\cdot\Delta\boldsymbol{\mu}_c|^2)^{1/2} \tag{16}$$

where $V_{\alpha\beta}$ is the translational inequivalent intermolecular interaction and $\Delta\boldsymbol{u}_c$ is the unit cell dipole moment change on excitation. A measurement of $\Delta\nu(\boldsymbol{F})$ versus $\boldsymbol{F}$ thus enables one to measure $V_{\alpha\beta}$ and $\Delta\boldsymbol{u}_c$ [23]. The observed large dipole moment changes for 9,10-dichloroanthracene [24] and anthracene-PMDA [25] confirmed speculation that the corresponding optical transitions in these solids were due to charge transfer excitations. In a recent paper by Veenvliet and Wiersma [26] the results of a combined Stark-Zeeman effect measurement on the lowest triplet state of p-benzoquinone-d_4 crystals were reported. These experiments clearly demonstrated the effect of the combined selection rules imposed on the system by Equations (10a), (10b) and (15) and analysis of the results enabled measurement of the factor group splitting in the spin-space forbidden origin and gave further strong support to the assignment of this state as a g-inversion level.

Finally we expect future applications of the Stark effect to include detailed study of interference spectra of polar

molecules and also exploitation of the Stark switching technique [27], in the study of coherent phenomena (using c.w. dye lasers) of molecular solids at low temperatures.

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Vibronische Wechselwirkungen zwischen beinahe entarteten Elektronenzuständen: Stark-Spektren von 2,6-p-Benzochinon-d_2

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Absorptionsspektren, von Kristallen, sichtbar und ultraviolett / Dipolmoment / Stark-Effekt / Vibronische Wechselwirkungen / Wellenfunktionen

Messungen des Stark-Effekts können zur Untersuchung vibronischer Wechselwirkungen benutzt werden. Die Anwendung dieser Methode auf die $n-\pi^*$-Übergänge von Chinonen wird diskutiert. Asymmetrische isotopische Sustitution kann in diesem Fall zu einer großen elektronischen Dissymetrie führen.

Stark spectroscopy can be used for the investigation of vibronic coupling between nearby electronic states. The application of this technique to the $n-\pi^*$ spectra of Quinones is discussed. Asymmetric isotopic substitution may, in this case, lead to a large asymmetry of the electronic wavefunction.

Die Messung spektraler Änderungen im elektrischen Feld erlaubt es, Dipolmomente und Polarisierbarkeiten im angeregten Zustand zu bestimmen, und gibt ein Gefühl für die Ladungsverteilung und damit für die elektronische Wellenfunktion dieses angeregten Zustandes. Die Elektronenspektren von Molekülkristallen (reine Kristalle oder Mischkristalle) bei tiefen Temperaturen besitzen im allgemeinen für die niedrigsten angeregten Zustände eine gut aufgelöste Schwingungsstruktur, die es gestattet, den Stark-Effekt an einzelnen Schwingungsbanden zu messen. Messungen an Molekülkristallen bieten den Vorteil, auch größere Moleküle untersuchen zu können, die für Messungen im Dampfzustand ungeeignet sind (zu niedriger Dampfdruck, schlechte spektrale Auflösung). Es ist weiter möglich, wesentlich höhere Felder als im Dampfzustand anzulegen und damit kleinere Effekte zu beobachten. Der wesentliche Nachteil besteht in der ungenügenden Kenntnis des lokalen Feldes [1]. Dieser Nachteil fällt aber nicht ins Gewicht für Messungen, bei denen die Abhängigkeit der Feldeffekte von verschiedenen Zuständen des gleichen Moleküls bestimmt werden soll, da man annehmen kann, daß das lokale Feld zumindest für verschiedene Schwingungszustände des gleichen Elektronenniveaus konstant bleibt.

Eine besonders interessante Anwendung für diesen Fall bieten Moleküle mit nahezu entarteten Elektronenzuständen. Die übliche Annahme, daß die Abhängigkeit der elektronischen